Preparation of Co-Added β -FeSi₂ by Cation-Exchange Reaction between Molten Salts and Si

Motohiro Sakamoto^{1,*} and Kazuki Morita²

¹Department of Materials Engineering, Graduate School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan

²Institute of Industrial Science, The University of Tokyo, Tokyo 153-8505, Japan

A β -Fe_(1-x)Co_xSi₂ film was prepared by a cation-exchange reaction between molten NaCl-KCl-FeCl₂-CoCl₂ salts and a Si substrate at 1173 K. At low CoCl₂ concentrations of molten salts, the β -FeSi₂ phase was formed. However, when the CoCl₂ concentration was higher than 0.015 mol%, α -FeSi₂ and FeSi phases were formed in addition to the β -FeSi₂ phase. The α -FeSi₂ and FeSi phases changed to β -FeSi₂ when the sample was annealed at 1123 K for 24 h. The Co content of the reaction layer increased with the CoCl₂ concentration of molten salts. The electrical resistivity of β -FeSi₂ was measured by the four-probe method, and the band gap (E_g) of the sample was roughly determined from the temperature dependence of electrical resistivity by using the equation $\rho = \rho_0 \exp(E_g/2kT)$. The electrical resistivity decreased and the band gap slightly decreased with the increase in the Co content of β -FeSi₂. [doi:10.2320/matertrans.M2009305]

(Received September 7, 2009; Accepted October 22, 2009; Published December 9, 2009)

Keywords: β -FeSi₂, cobalt, molten salts, exchange reaction, silicides, electrical resistivity

1. Introduction

β -FeSi₂ is a semiconductor with a direct band gap of approximately 0.85 eV and has a larger absorption coefficient (approximately 10^5 cm^{-1} at 1 eV)^{1,2)} than other semiconductors. It has also been reported that β -FeSi₂ can be grown on a Si substrate epitaxially.³⁾ Due to these characteristics, β -FeSi₂ could be used in the fabrication of photovoltaic cells and light emitting diodes (LEDs) on a Si substrate. FeSi₂ exists in two main stable phases: the semiconducting orthorhombic β -FeSi₂ phase, which is stable below 1255 K and the metallic tetragonal α -FeSi₂ phase, which is stable above 1210 K.⁴⁾ Therefore, it is impossible to prepare β -FeSi₂ directly from Fe-Si binary liquids. The β -FeSi₂ layer can be fabricated on a Si substrate by using various techniques such as the ion-beam synthesis (IBS) method,⁵⁾ multilayer technique,³⁾ and reactive deposition epitaxy (RDE).⁶⁾ However, these physical vapor deposition (PVD) methods are not suitable for mass production for photovoltaic cells, because a vacuum atmosphere is required to fabricate β -FeSi₂ and the deposition rate is extremely low.

Yoneyama *et al.* developed a new preparation method to overcome these problems.⁷⁾ They focused on the cation-exchange reaction between a Si wafer and FeCl₂ in NaCl-KCl-FeCl₂ molten salts and succeeded in fabricating a β -FeSi₂ layer with a thickness of approximately 5~10 μm on a Si substrate. For the β -FeSi₂ film prepared by the chemical reaction given in eq. (1), the growth rate was higher than the films fabricated by other preparation methods; in addition, a vacuum atmosphere was not required for this method.

Numerous researches have been carried out on the modification of the properties of β -FeSi₂, such as conductivity and band gap by adding a third element such as Co or Ni in order to enable the use of β -FeSi₂ in optoelectronic devices. According to Panknin *et al.*, the electrical resistivity

as well as the energy of the direct band gap of the β -Fe_(1-x)Co_xSi₂ layer decreases with increasing Co content of β -Fe_(1-x)Co_xSi₂. Thus, the band gap could be controlled between 0.84 eV and 0.70 eV.⁸⁾ However, the process of fabrication of the β -Fe_(1-x)Co_xSi₂ layer on the Si substrate by ion implantation was complicated because this fabrication process involved a large number of steps. First, Fe was implanted in the Si substrate, and then, the substrate was annealed so as to form the required structure, i.e., a β - or α -FeSi₂ phase. Second, Co was implanted in the substrate, and the substrate was annealed in order to stabilize the β -FeSi₂ phase. Therefore, a simpler method to prepare a β -Fe_(1-x)Co_xSi₂ layer on a Si substrate was required.

In this study, a Co-added β -FeSi₂ layer was prepared by a cation-exchange reaction between Si and molten NaCl-KCl-FeCl₂-CoCl₂ salts. In addition, the temperature dependence of the resistivity of the β -FeSi₂ layer was investigated to evaluate the properties of the prepared sample.

2. Experimental Procedure

Molten salt was prepared by adding FeCl₂ and CoCl₂ to a NaCl-50 mol% KCl salt. Reagent-grade NaCl, KCl, FeCl₂·4H₂O, and CoCl₂·6H₂O were weighed and mixed together. The total amount of chlorides was fixed to 3.5 g. Table 1 lists the concentration values of chlorides used in the experiments. Prior to the experiments, the chlorides were preliminarily melted at 1173 K for 30 min under a helium

Table 1 Concentration of chloride used in experiments.

Sample	Concentration (mol%)			
	FeCl ₂	CoCl ₂	NaCl	KCl
FC-00	0.100	0	49.95	49.95
FC-05	0.095	0.005	49.95	49.95
FC-10	0.090	0.010	49.95	49.95
FC-15	0.085	0.015	49.95	49.95
FC-20	0.080	0.020	49.95	49.95

*Graduate Student, The University of Tokyo

Table 2 Change in concentration of chloride (FC-20) due to preliminary melting.

FC-20	Concentration (mol%)			
	FeCl ₂	CoCl ₂	NaCl	KCl
Before melting	0.080	0.020	49.95	49.95
After melting	0.0705	0.0120	53.5	46.4

Fig. 1 Schematic diagram of experimental apparatus.

atmosphere to form the NaCl-KCl-FeCl₂-CoCl₂ salt. Table 2 lists the changes in the chloride concentration of the FC-20 sample measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) during preliminary melting. The FeCl₂ concentration hardly changed, whereas the CoCl₂ concentration reduced by half in the preliminarily melted salt. CoCl₂ in the molten salts appeared to evaporate from the molten salt to the gas phase.

A p-type Si(100) wafer ($\rho > 1000 \Omega\cdot\text{cm}$; $10 \times 10 \times 0.5 \text{ mm}^3$) was used as the substrate. The Si wafer was cleaned by the RCA method, and a thin protective oxide layer was etched in a HF solution (HF : H₂O = 1 : 1). Figure 1 shows a schematic diagram of the experimental apparatus. The Si substrate and the NaCl-KCl-FeCl₂-CoCl₂ salt were placed in a graphite crucible. Titanium powder, which acts as a deoxidizing agent, was placed in another graphite crucible. These two crucibles were placed in a quartz reaction tube. After evacuating the quartz tube, helium gas was introduced into it. The reaction tube was placed in a furnace kept at 1173 K for 3 h, and then, the tube was withdrawn from the furnace and cooled to room temperature in air. After separating the substrates from the salts, the substrates were annealed at 1123 K in a helium atmosphere for 6 or 24 h.

The layers formed by the reactions in the reaction tube were characterized by X-ray diffraction (XRD) measurements, and their chemical composition was analyzed by an

Table 3 Phases detected by XRD analysis before annealing.

Sample	After Reaction
FC-00	β -FeSi ₂
FC-05	β -FeSi ₂
FC-10	β -FeSi ₂
FC-15	β -FeSi ₂ + α -FeSi ₂ + FeSi
FC-20	β -FeSi ₂ + α -FeSi ₂ + FeSi

Fig. 2 XRD patterns of samples after experiments: (a) FC-05 and (b) FC-20.

electron probe microanalyzer (EPMA). The resistivity of the grown layers was measured by the four-probe method.

3. Results and Discussion

3.1 Phases formed under different CoCl₂ contents in molten salts

Table 3 lists the results of the XRD measurement of samples before they were annealed. When the CoCl₂ concentration of the salt was less than 0.010 mol% (See Fig. 2(a)), only the β -FeSi₂ phase was formed on the Si wafer. When the CoCl₂ concentration was higher than 0.015 mol%, α -FeSi₂ and FeSi phases were formed together with the β -FeSi₂ phase (Fig. 2(b)).

In the reaction between the Si wafer and the molten NaCl-KCl-FeCl₂-CoCl₂ salts, Co and Fe simultaneously reacted to form β -Fe_(1-x)Co_xSi₂. On the other hand, as CoCl₂ content of the molten salts increased, it was found that α -FeSi₂ was also formed. In general, it is known that α -FeSi₂ becomes unstable at temperatures lower than 1210 K. The formation of α -FeSi₂ may be caused by the increasing Co content of β -FeSi₂ with the increase of CoCl₂ content of molten salts. The stabilization of α -FeSi₂ with the increase of Co content can be supported by the research of Wieser *et al.*⁹⁾ They reported that the phase-transformation temperature from β -FeSi₂ to α -FeSi₂ decreases with an increase in the Co content of β -Fe_(1-x)Co_xSi₂. According to them, the phase-transformation temperatures for Fe_{0.9}Co_{0.1}Si₂ and Fe_{0.8}Co_{0.2}Si₂ are $1198 \pm 25 \text{ K}$ and $1148 \pm 25 \text{ K}$, respectively. Increasing Co content with the increase of CoCl₂ content of molten salt was

Table 4 Phases detected by XRD analysis after annealing at 1123 K for 6 and 24 h.

Sample	Before annealing	After 6 h annealing	After 24 h annealing
FC-15	$\beta\text{-FeSi}_2 + \alpha\text{-FeSi}_2 + \text{FeSi}$	$\beta\text{-FeSi}_2 + \alpha\text{-FeSi}_2$	$\beta\text{-FeSi}_2$
FC-20	$\beta\text{-FeSi}_2 + \alpha\text{-FeSi}_2 + \text{FeSi}$	$\beta\text{-FeSi}_2 + \alpha\text{-FeSi}_2$	$\beta\text{-FeSi}_2 + \alpha\text{-FeSi}_2$

Table 5 Composition of the reaction layers of the samples annealed for 6 h at 1123 K measured by EPMA.

Sample	Composition (at%)			Si/(Fe + Co)
	Fe	Co	Si	
FC-00	33.3	—	66.6	2.0
FC-05	31.3	0.4	68.3	2.2
FC-10	31.7	1.0	67.2	2.1
FC-15	30.6	1.9	67.4	2.1
FC-20	28.8	2.6	68.7	2.2

confirmed by the EPMA (It was discussed following section).

Therefore, the samples prepared by using the molten salts with CoCl_2 concentrations of 0.015 mol% and 0.020 mol% were annealed at 1123 K in order to obtain the single $\beta\text{-FeSi}_2$ phase.

Table 4 lists the results of the XRD measurement of samples annealed at 1123 K for 6 and 24 h. The $\alpha\text{-FeSi}_2$ phase remained after annealing for 6 h. However, in the FC-15 sample, the $\alpha\text{-FeSi}_2$ phase completely changed to the $\beta\text{-FeSi}_2$ phase after annealing for 24 h at 1123 K. It appears that the $\beta\text{-FeSi}_2$ phase can be obtained by annealing at temperatures lower than 1123 K.

3.2 Dependence of Co content of reaction layer on CoCl_2 concentration of molten salt

The Fe, Co and Si contents of the reaction layers of the samples annealed for 6 h were measured by EPMA (Table 5). The ratio between Si content and total content of Fe and Co was close to 2.0. By this result and XRD analysis, the reaction layer was confirmed to be α - or $\beta\text{-Fe}_{(1-x)}\text{Co}_x\text{Si}_2$. Co content of the reaction layer, x ($\text{Fe}_{(1-x)}\text{Co}_x\text{Si}_2$) was calculated from this result. Figure 3 shows the relationship between the Co content, x , and the CoCl_2 concentration of the molten salts. The Co content of $\beta\text{-FeSi}_2$ increases with an increase in the CoCl_2 concentration of the molten salts. It is possible to control the Co content of $\beta\text{-FeSi}_2$ by changing the CoCl_2 concentration of the molten salt.

The concentrations of CoCl_2 and FeCl_2 in the salt after the experiments were measured by ICP-AES (Table 6). It was confirmed that a small amount of FeCl_2 and CoCl_2 remained in the salt after the experiments. Assuming that the entire amount of FeCl_2 and CoCl_2 was consumed to form the $\beta\text{-Fe}_{(1-x)}\text{Co}_x\text{Si}_2$ layer, the Co content, x , of $\beta\text{-Fe}_{(1-x)}\text{Co}_x\text{Si}_2$ was evaluated, as listed in Table 6; these values of the Co content were much higher than those measured by using the EPMA. This is because some amount of CoCl_2 in the chloride evaporated to the gas phase during preliminary melting and some amount reacted with the Si wafer, as described in the experimental procedure; therefore, the amount of CoCl_2 served to the reaction reduced by evaporation.

Fig. 3 Relationship between Co content of reaction layer, x ($\text{Fe}_{(1-x)}\text{Co}_x\text{Si}_2$) and CoCl_2 concentration of molten salts.

3.3 Temperature dependence of electrical resistivity

To confirm the influence of Co added by the molten salts on the physical properties of $\beta\text{-FeSi}_2$, the electrical resistivity of $\beta\text{-FeSi}_2$ on the Si wafer was measured by the four-probe method. The logarithmic values of the resistivity of the FC-00, FC-05, and FC-10 samples, which were annealed for 6 h to be the single phase, were plotted against the reciprocal of the absolute temperature (Fig. 4). The resistivity decreased as the Co content of $\beta\text{-FeSi}_2$ increased. It was also observed that the slope of the plot of each sample changed at a certain temperature. That is, the electrical resistivity of $\beta\text{-FeSi}_2$ exhibits extrinsic behavior at low temperatures and intrinsic behavior at high temperatures. At low temperatures, carriers which conducted in the $\beta\text{-FeSi}_2$ film were caused by the activation from the impurity level to the conduction (valence) band. For the FC-05 and FC-10 samples, the conductive activation energy (E_p) was calculated by using eq. (2)¹⁰ and the slope of the plots in Fig. 4.

$$\ln \rho = C - \frac{E_p}{kT} \quad (2)$$

where k and C denote the Boltzmann's constant and the temperature-independent constant, respectively. The activation energies of the samples were calculated to be 0.056 eV for the FC-05 sample ($x = 0.013$ in $\beta\text{-Fe}_{(1-x)}\text{Co}_x\text{Si}_2$) and 0.030 eV for the FC-10 sample ($x = 0.032$). Tani *et al.* reported that the conductive activation energy of $\beta\text{-Fe}_{(1-x)}\text{Co}_x\text{Si}_2$ is 0.054 eV for $x = 0.01$ and 0.034 eV for $x = 0.03$;¹⁰ these values are in good agreement with the values obtained by us.

The temperature dependence of electrical resistivity at high temperatures can be attributed to the activation of carriers from the valence (conduction) band to the conduction (valence) band. The temperature dependence of resistivity at these temperatures can be expressed as follows:

Table 6 Concentration of chloride after experiments and calculated and measured Co content of reaction layer, x ($\text{Fe}_{(1-x)}\text{Co}_x\text{Si}_2$).

Sample	Concentration (mol%)				Co content, x	
	FeCl ₂	CoCl ₂	NaCl	KCl	Calculated	Measured by EPMA
FC-00	6.55×10^{-4}	ND	53.6	46.4	0	0
FC-05	9.18×10^{-4}	ND	53.3	46.7	0.05	0.013
FC-10	6.84×10^{-4}	3.67×10^{-4}	52.8	47.2	0.10	0.032
FC-15	4.29×10^{-4}	ND	53.1	47.0	0.15	0.059
FC-20	5.62×10^{-4}	5.43×10^{-4}	52.8	47.1	0.20	0.082

Fig. 4 Temperature dependence of electrical resistivity of samples.

$$\ln \rho = C' - \frac{E_g}{2kT} \quad (3)$$

where E_g and C' denote the band gap of samples and the temperature-independent constant, respectively. The band gaps of the FC-00, FC-05, and FC-10 samples were calculated by using the above equation and were found to be 0.98, 0.92, and 0.86 eV, respectively; these values indicated that the band gap decreased as the Co content of β -Fe_(1-x)Co_xSi₂ increased. As mentioned above, the amount of Co added to β -FeSi₂ by the cation-exchange reaction with molten salts influenced the physical properties of β -FeSi₂, such as the electrical resistivity and band gap.

However, the band gap values obtained in this study are higher than the reported values (approximately 0.85 eV) measured by infrared transmission and reflection measurements.^{1,2,7)} Both β -FeSi₂ and Si are semiconductors, and the band gap of Si (~ 1.1 eV) is larger than that of β -FeSi₂. At high temperatures, the value of electrical resistance of the Si substrate neared that of β -FeSi₂. The band gap values of β -FeSi₂ obtained by the four-probe method at high temperatures were larger than those obtained by infrared transmission and reflection measurements because of the influence of the Si substrate.

4. Conclusion

A Co-added β -FeSi₂ film was prepared by a cation-exchange reaction between molten NaCl-KCl-FeCl₂-CoCl₂ salts and a Si wafer. When the concentration of CoCl₂ was less than 0.010 mol%, the β -FeSi₂ phase was obtained. When the concentration of CoCl₂ was higher than 0.015 mol%, α -FeSi₂ and FeSi phases were formed in addition to the β -FeSi₂ phase. When the sample prepared by using molten salts with a CoCl₂ concentration of 0.015 mol% (FC-15) was annealed for 24 h at 1123 K, a single β -FeSi₂ layer was obtained. The Co content of β -FeSi₂ increased with the CoCl₂ concentration of the molten salts. The resistivity and band gap of β -FeSi₂ decreased as the Co content of β -Fe_(1-x)Co_xSi₂ increased.

Acknowledgment

We would like to thank Prof. H. Inoue and Dr. A. Masuno, Institute of Industrial Science, The University of Tokyo, for their kind assistance in the characterization of the samples.

REFERENCES

- 1) K. H. Tan, D. Z. Chi and K. L. Pey: J. Appl. Phys. **104** (2008) 064117.
- 2) Z. Yang, K. P. Homewood, M. S. Finney, M. A. Harry and K. J. Reeson: J. Appl. Phys. **78** (1995) 1958.
- 3) T. Suemasu, N. Hiroi, T. Fujii, K. Takakura and F. Hasegawa: Jpn. J. Appl. Phys. **38** (1999) L878.
- 4) H. Okamoto: *Phase Diagrams of Binary Iron Alloy*, (ASM International, Ohio, 1993) p. 380.
- 5) Y. Maeda, K. Umezawa, Y. Hayashi, K. Miyake and K. Ohashi: Thin Solid Films **381** (2001) 256.
- 6) T. Suemasu, M. Tanaka, T. Fujii, S. Hasimoto, Y. Kumagi and F. Hasegawa: Jpn. J. Appl. Phys. **36** (1997) L1225.
- 7) T. Yoneyama, T. Yoshikawa and K. Morita: Jpn. J. Appl. Phys. **46** (2007) 5233.
- 8) D. Pankin, E. Wieser, W. Skorupa, W. Henrion and H. Lange: Appl. Phys. A **62** (1996) 155.
- 9) E. Wieser, D. Panknin, W. Skorupa, G. Querner, W. Henrion and J. Albrecht: Nucl. Instrum. Methods B **80/81** (1993) 867.
- 10) J. Tani and H. Kido: J. Appl. Phys. **84** (1998) 1408.